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# Q&A

Roger Lohman



## Could you provide information on bonding plastics?

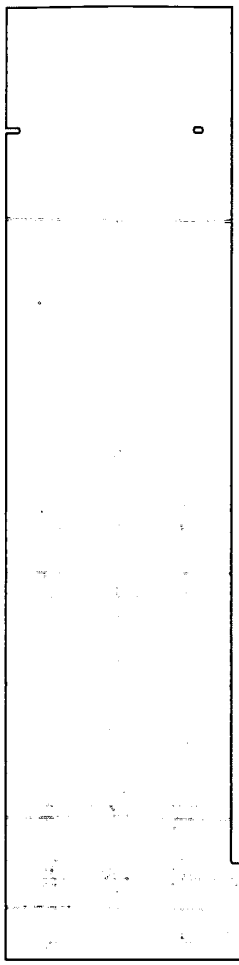
We receive numerous questions pertaining to bonding plastics with little or no further details. Since the term plastic is so generic, it must be defined more specifically. The necessity of specifying the exact plastic is paramount due to differences in surface energies. As a general rule, the lower the surface energy of the solid, the more difficult it may be to bond using an adhesive. In comparing plastics to metals, the surface energy of plastics may often be 20 to 40 times less than that of metal. For example, the surface energy of aluminum is above 800 dynes/cm, and copper is above 1,100 dynes/cm. Plastics fall below 100 dynes/cm and most below 50 dynes/cm. As a general rule, the greater the hardness and the higher the melting point, the higher the surface energy. Thus, the softer organic solids have much lower melting points and corresponding far lower surface energies.

This same concept of low surface energy is used in mold-release agents whereby a thin film is sprayed onto the mold. In this case, these mold-release agents have surface energies generally in the range of 10 to 24 dyne/cm. Let's compare this to various plastics as shown in the table.

As seen from this table, the spread between these plastics could be considered not all that great especially when considering that metals are in the 800+ range and glass is between 300-500 dynes/cm. But as practice tells us, it is far easier to bond ABS than polyethylene with adhesives even though they are only 11 dynes/cm apart from each other in surface energy. This is why it is so important to be specific about the type of plastic being bonded.

The numbers shown in the table are without any pretreatment to the plastic. Sandblasting, etching or corona treatment will of course drastically affect the bond strengths with adhesives. Therefore, the evaluation of any adhesive must also take into account the costs related to pretreatment. In the past year, at least one new adhesive has been introduced that requires no pretreatment for bonding to polyethylene or polypropylene.

-ROGER LOHMAN



**Surface / Surface Energy (dynes/cm)**

Polytetrafluoroethylene (Teflon) -- 18

Polypropylene -- 29

Polyethylene -- 31

Polystyrene -- 33

Polyvinyl chloride -- 39

ABS -- 42

Polycarbonate -- 42

Polyethylene Terephthalate -- 43

Nylon 6,6 -- 43

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PLASTICS CONSULTANCY NETWORK

# Corona Discharge

**by Peter Prentice - PolyTech Consultants**

## Introduction

Low energy plastics, such as polypropylene (PP), polyethylene (PE) and Teflon (PTFE) are essentially "non- stick" plastics. Their molecular structure inhibits the adhesion and printing processes - this molecular structure is basically inert or inactive – these polymers are said to have a low surface energy.

The surface energy or the wetability of a particular substrate is measured in dynes/cm (or ergs/cm$^2$) and, when tested, untreated PP and PE will have a low surface energy (usually 30 to 32 dynes/cm). The most common method of determining the surface energy is to measure the contact angle of a water droplet on the substrate surface. The contact angle between the solid and the fluid is the angle measured within the fluid, between the solid surface and the tangent plane to the liquid surface at the point of intersection (see Figure 1 below). A contact angle of greater than 90° indicates that the fluid (which is ink or adhesive in this case) has not wet the surface. Conversely an angle of less than 90° means that the fluid has wet the surface - if the angle approaches zero then the surface is completely wetted by the fluid.

Use of a corona, flame or other surface treatment will raise the surface energy level to values in excess of 42 dynes/cm. Ideally, the surface energy of the plastic should be 7 to 10 dynes/cm higher than the surface tension of the solvent or liquid. For example, a printing ink having a surface tension of 30 dynes/cm would not adequately wet or bond to a material having a surface energy less than 37 to 40 dynes/cm .

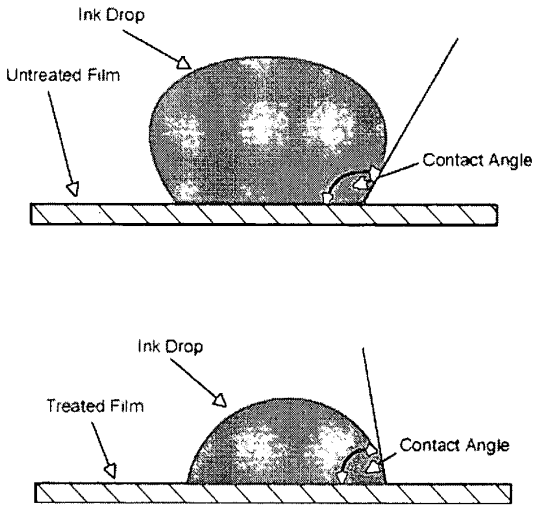



Figure 1 Schematic Representation of Surface Tension

**Corona Discharge** treatment is the most common method of increasing the energy level of PP and PE materials (see below). This process uses an electric current to create an ozone generating spark - a corona. The ozone within the corona reacts with the PP or PE surface to raise the energy level. While this method is very popular, it is not long lasting and the increase in the surface energy can disappear within weeks.

A corona treatment system in its simplest form can be thought of as a capacitor. Voltage is applied to

the top plate which, in the case of corona treatment, would be the electrode (see Figure 2 below). The dielectric portion of the capacitor would be made up of some type of roll covering, air and the substrate (film or sheet). The final component, or bottom plate, would take the form of an electrically grounded roll. In the corona treatment system the voltage build-up ionises the air in the air gap creating a corona, which modifies the surface and increases the surface energy of the substrate passing over the electrically grounded roll. The level of treatment is controlled by the energy of the discharge and the air gap. For health and safety reasons, the ozone generated in the corona must be removed from the working environment.

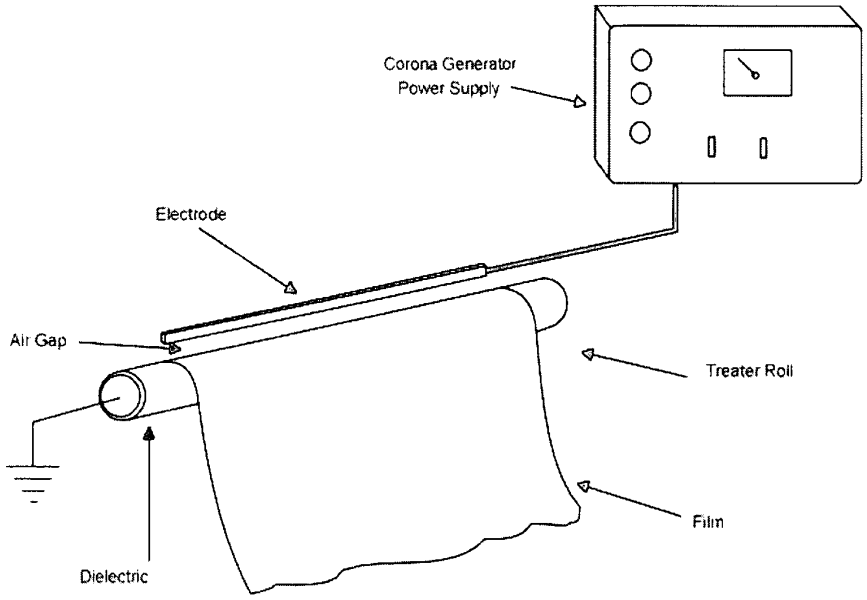



Figure 2 Corona Treatment System

The corona treatment system is introduced into the film blowing equipment usually at the top of the tower (see Figure 3 below), but not always. Some systems incorporate the treatment midway up the tower or at the base.

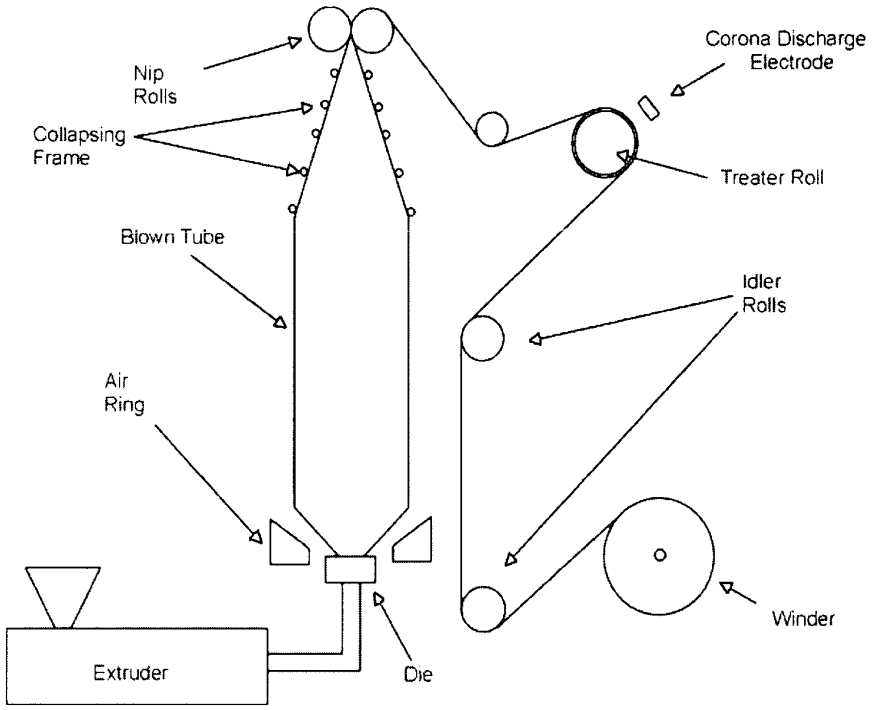



Figure 3 Line Schematic – Top of the Tower Treatment

Similarly, the corona treatment system would be included in the line of an extruded sheet line (see Figure 4) and stentered film .

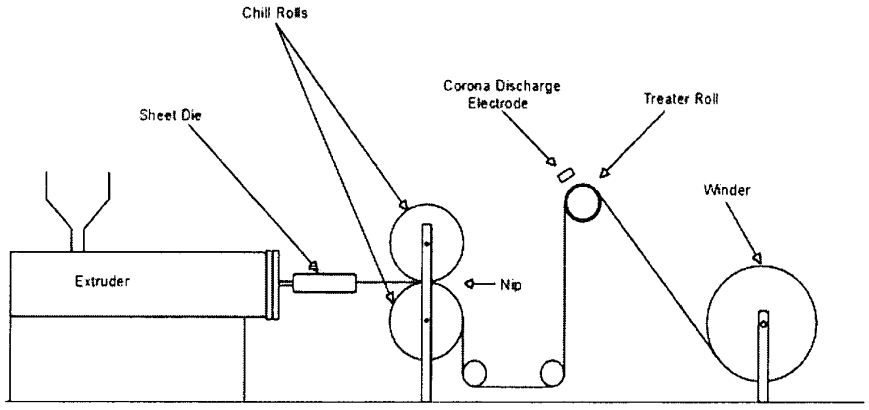



Figure 4 Sheet Extrusion Line

**Backside Treating** of the web occurs when the corona (oxidised air) is present at the surface of the material. So, if the wrap is insufficient on the treater roll (see Figure 5 below), backside treatment will occur. Solutions to backside treatment range from ensuring that there is more wrap on the roll to the use of nip rolls.

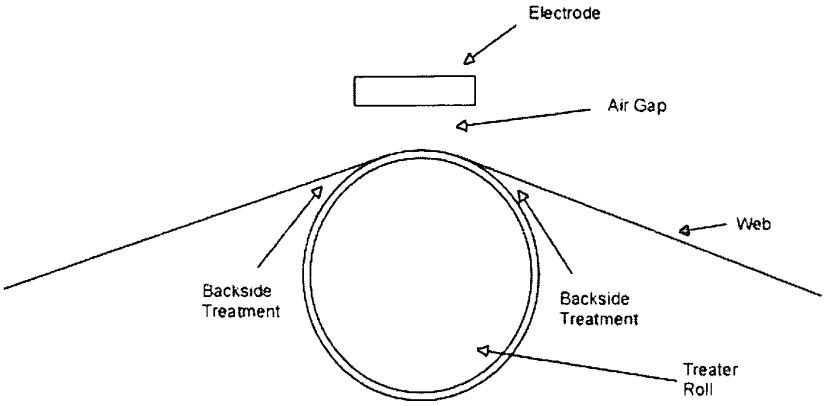



Figure 5 Insufficient Wrap leads to Backside Treatment

**Flame** treatment is also a common method of increasing the energy level of PP and PE materials. This process uses an oxygenated flame to create free oxygen. This free oxygen then reacts with the surface of the PP or PE and raises the surface energy level. As with corona treatment, this method is not long lasting and can disappear within weeks.

## Problems you might find

**Blocking.** The greater the level of treatment, the higher the degree of oxidation of the surface. The polar groups formed by the corona have an attraction for the molecular layer on the other side of the web, and when the two sides come into contact when they are on the roll, a self-adhering condition exists. Sometimes this attraction can be greater than the internal bonds of the substrate so that delamination of the substrate can occur when the product is unrolled. The tighter the roll is wound and the longer it is in storage the more severe the problem becomes. Blocking is worse in the film at the centre of the roll.

**Heat Sealing.** Excessive treatment also leads to problems when attempting to heat seal the product.

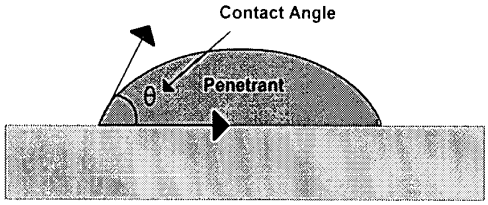
**Additives**. If the polypropylene or polyethylene contain additional components, such as slip additives or some processing aids, the initial treatment is reduced over time as these additives bloom to the surface and partially mask the polar groups formed during treatment. For this reason, it is better to treat these films at the point of use rather than the point of manufacture.

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# Surface Energy (Surface Wetting Capability)

As previously mentioned, one of the important characteristics of a liquid penetrant material is its ability to freely wet the surface of the object being inspected. At the liquid-solid surface interface, if the molecules of the liquid have a stronger attraction to the molecules of the solid surface than to each other (the adhesive forces are stronger than the cohesive forces), then wetting of the surface occurs. Alternately, if the liquid molecules are more strongly attracted to each other and not the molecules of the solid surface (the cohesive forces are stronger than the adhesive forces), then the liquid beads-up and does not wet the surface of the part.

One way to quantify a liquid's surface wetting characteristics is to measure the contact angle of a drop of liquid placed on the surface of the subject object. The contact angle is the angle formed by the solid/liquid interface and the liquid/vapor interface measured from the side of the liquid. See the figure below. Liquids wet surfaces when the contact angle is less than 90 degrees. For a penetrant material to be effective, the contact angle should be as small as possible. In fact, the contact angle for most liquid penetrants is very close to zero degrees.




Wetting ability of a liquid is a function of the surface energies of the solid-gas interface, the liquid-gas interface, and the solid-liquid interface. The surface energy across an interface or the surface tension at the interface is a measure of the energy required to form a unit area of new surface at the interface. The intermolecular bonds or cohesive forces between the molecules of a liquid cause surface tension. When the liquid encounters another substance, there is usually an attraction between the two materials. The adhesive forces between the liquid and the second substance will compete against the cohesive forces of the liquid. Liquids with weak cohesive bonds and a strong attraction to another material (or the desire to create adhesive bonds) will tend to spread over the second material. Liquids with strong cohesive bonds

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and weaker adhesive forces will tend to bead-up or form a droplet when in contact with the second material.

In liquid penetrant testing, there are usually three surface interfaces involved, the solid-gas interface, the liquid-gas interface, and the solid-liquid interface. For a liquid to spread over the surface of a part, two conditions must be met. First, the surface energy of the solid-gas interface must be greater than the combined surface energies of the liquid-gas and the solid-liquid interfaces. Second, the surface energy of the solid-gas interface must exceed the surface energy of the solid-liquid interface.

A penetrant's wetting characteristics are also largely responsible for its ability to fill a void. Penetrant materials are often pulled into surface breaking defects by capillary action. The capillary force driving the penetrant into the crack is a function of the surface tension of the liquid-gas interface, the contact angle, and the size of the defect opening. The driving force for the capillary action can be expressed as the following formula:

$$\text{Force} = 2\pi r\sigma_{LG}\cos\theta$$

Where:

r = radius of the crack opening (2pr is the line of contact between the liquid and the solid tubular surface.)
$\sigma_{LG}$ = liquid-gas surface tension
$\theta$ = contact angle

Since pressure is the force over a given area, it can be written that the pressure developed, called the capillary pressure, is

$$\text{Capillary Pressure} = (2\sigma_{LG}\cos\theta)/r$$

The above equations are for a cylindrical defect but the relationships of the variables are the same for a flaw with a noncircular cross section. Capillary pressure equations only apply when there is simultaneous contact of the penetrant along the entire length of the crack opening and a liquid front forms that is an equidistant from the surface. A liquid penetrant surface could take-on a complex shape as a consequence of the various deviations from flat parallel walls that an actual crack could have. In this case, the expression for pressure is

$$\text{Capillary Pressure} = 2(\sigma_{SG} - \sigma s_{SL})/r = 2\Sigma/r$$

Where:

$\sigma_{SG}$ = the surface energy at the solid-gas interface.
$\sigma_{SL}$ = the surface energy at the solid-liquid interface.
r = the radius of the opening.
$\Sigma$ = the adhesion tension ($\sigma_{SG} - \sigma_{SL}$).

Therefore, at times, it is the adhesion tension that is primarily responsible for a penetrant's movement into a flaw and not the surface energy of the liquid-gas interface. Adhesion tension is the force acting on a unit length of the wetting line from the direction of the solid. The wetting performance of the penetrant is degraded when adhesion tension is the primary driving force.

It can be seen from the equations in this section, that the surface wetting characteristics (defined by the surface energies) are important penetrant characteristics for filling the flaw. The liquid penetrant will continue to fill the void until an opposing force balances the capillary pressure. This force is usually the pressure of trapped gas in the void as most flaws are open only at the surface of the part. Since the gas originally in the flaw volume cannot escape through the layer of penetrant, the gas is compressed near the closed end of the flaw.

Since the contact angle for penetrants is very close to zero, other methods have been devised to make relative comparisons of the wetting characteristics of these liquids. One method is to measure the height that a liquid reaches in a capillary tube. However, the solid interface in this method is usually glass and may not accurately represent the surface that the penetrant inspection will be performed on. Another method of comparative evaluation is to measure after a set time has elapsed, the radius, the diameter, or the area of a spot formed when a drop of penetrant is placed on the test surface. However, using this method, other factors are also acting in the comparison. These methods include the density, viscosity, and volatility of the liquid, which do not enter into the capillarity equations, but may have an effect on the inspection as discussed in the related pages.

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# Dynamic Surface Tension and Surface Energy in Ink Formulations and Substrates

**It is essential that ink formulators understand the principles and relationships of surface tension, and surface energy or "wetting tension." They must control coating transfer and adhesion by developing formulations that perform well under widely varying application speeds and operating conditions. There are factors that can be controlled, and others that cannot be controlled. A review of these principles and relationships, with a brief introduction to formulation variables, will reinforce the knowledge that it takes to mitigate, or entirely avoid, coating problems.**

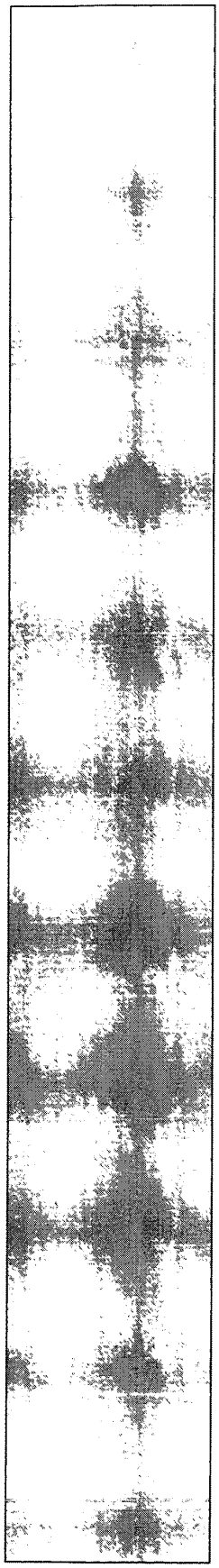
Solventborne formulations, with their naturally lower surface tensions, wet readily and transfer well onto most substrates, even though they may have higher coefficients of spreading on select substrates. The increasing shift to waterborne ink, due to environmental concerns, has inherent problems of surface wetting, foaming, and flow and leveling, common to all waterborne systems. Waterborne inks require alcohols and surfactants to lower their surface tensions to acceptable levels for transfer, spreading and adhesion.

Alcohols have low surface tensions and are "non-active," but most common surfactants used in waterborne systems generally have high surface activity that varies with changes in concentration, molecular weight and structure. A coating application is a dynamic process, and active surfactants cause surface tensions to change as speeds and formulations change. Surfactant activity directly impacts coating spread and adhesion. The surface tension of inks must be lower than the wetting tension of substrates to attain good printability, adhesive bondability, or ink lay down.

## Formulation Changes

Formulation and application of waterborne ink are influenced somewhat by controllable, external factors, such as shipping and storage, freezing and thawing, both before and after each process takes place. The physical properties of handling and mixing systems, to a large degree, are fixed and uncontrollable. Many facilities suffer the uncontrollable effects of seasonal changes — hot summer vs. cold winter environments, for example. Inks can and often do change at the formulation site, and change even more just prior to, and during, application. What is often formulated and tested in the laboratory is not what is ultimately used during application. Alcohols and reagents are lost to evaporation, and these losses can go undetected unless testing can be done at formulation and process sites.

When any ink or coating is applied, surfactant molecules in the bulk solution react by diffusing to the interface. It is at this interface that the surfactant molecules try to line up with their hydrophobic ends pointed at the interface and the surface tension is lowered. The concentration and nature of the



and the surface tension is lowered. The concentration and nature of the surfactant determines how much the surface tension can be reduced, but the speed at which diffusion takes place influences how fast wetting will occur. Wetability, and ultimately "coatability," is influenced by the combined physical and chemical properties of the constituents. This article will examine the area of controllable factors, with emphasis on techniques used to measure the dynamic surface tension of inks and the wetting tension of the solid surface (substrate) to be coated.

## Surface Tension and Surfactants

Surface tension can be thought of as the force that "holds" a fluid together in the presence of air, within its own confines — the tangential intermolecular force of attraction between adjacent molecules. Surface tension dictates whether a coating will wet and spread over, or retract from, a solid surface. Surface tension is expressed as force per unit of width; as dynes/cm (or mN/m). Water has a high surface tension, in the range of 72 dynes/cm while alcohols are in a low range of 20 to 22 dynes/cm. Solvents, typically used in solventborne formulations, are in the 20–30 dynes/cm range. This is the major reason that substituting waterborne formulations, with their high inherent surface tension values, for much lower surface tension solventborne systems is a major challenge.

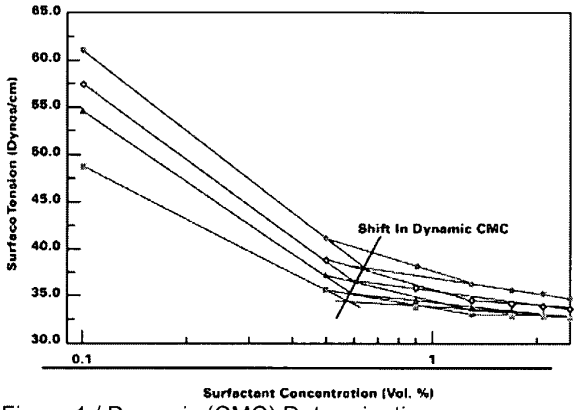
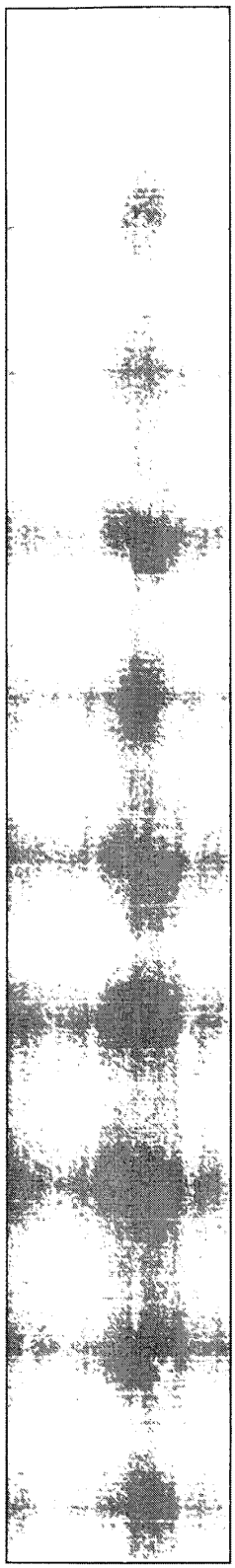


Figure 1 / Dynamic (CMC) Determination

Surfactants are used because of their ability to reduce surface tension. They are classified by the ionic charge of the surface acting part of the molecule. Anionic surfactants have a negative molecular charge, cationics positive, and nonionics no charge. Amphoterics have both positive and negative charges. Anionics and nonionic surfactants provide most of industrial surfactant requirements. Selection of surfactants is based on specific needs and often mixed surfactants are used.

In general, surfactants with a smaller (lighter) molecule mass (short hydrophobic tail) diffuse more rapidly to the interface, and are vertically adsorbed at the interface, causing a compressive force to act on the surface thereby reducing surface energy or surface tension. Nonionic surfactants with ethylene oxide groups usually diffuse very rapidly to the surface while fluorinated surfactants are slower and more effective at equilibrium. Most surfactants at higher concentrations exert strong molecular attractions between adjacent molecules causing strong surface films, the strength of which determines the surface properties of the surfactant solutions.

At the instant a coating is deposited on a substrate, at zero time of new surface generation, the concentration of surface active molecules at the interface will be the same as in the bulk solution; equal to the surface tension of the pure solvent. The surfactant molecules then begin to diffuse to, and adsorb at, the newly created fluid/substrate interface and the fluid/air interface. It takes a finite amount of time for the surface tension to reach equilibrium, anywhere from several seconds to several minutes. This is why the relevant parameter in designing formulations is dynamic surface tension rather than static (also known as equilibrium) surface tension.



Surface tension dictates whether a coating will wet and spread over, or retract from, a solid substrate. Inks exhibit both an adhesive force that is a measurement of the degree of association of the coating for the substrate, and a cohesive force that is a measure of the degree of self-adhesion of the coating. Spreading coefficient is the difference between work of adhesion and work of cohesion. If work of adhesion is greater than work of cohesion then spontaneous spreading occurs. If work of cohesion is greater than work of adhesion, then retraction, a surface defect, occurs as the coating will preferentially associate with itself.

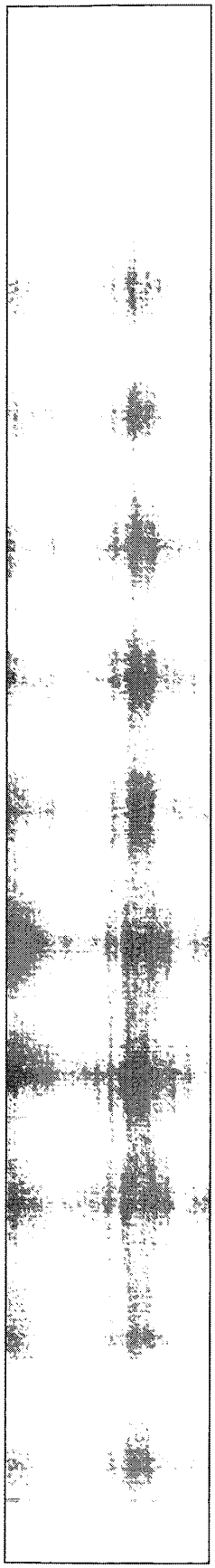
Classical belief is that many surface tension related properties such as detergency, foaming, and wetting, either maximize or minimize at the surfactant critical micelle concentration (CMC). These relationships, however, are based on classical measurements limited to static surface tension conditions, when equilibrium has been established between the surface layer and the bulk solution. Dynamic surface tension measurements of active surfactants reveal levels at which surfactant effectiveness is at its highest, which is not necessarily related to equilibrium CMCs. Dynamic measurements more accurately reflect actual, in-process, surfactant and coating performance. In effect, if you limit surfactant migration time (by using a faster coating process) you require more surfactant to perform the same job as in the slower process. Figure 1 illustrates a series of dynamic curves where the CMC point moves to the right (increasing concentration) as the curves move upward with decreasing surface age (decreasing surfactant migration time).

## Ink Formulation Variables

Waterborne systems have some inherent advantages over solventborne systems, such as lower resolubility rates and higher viscosities, but they are more pH sensitive. Common formulations often combine a soluble resin in a water-amine-emulsion system. Therefore, pH is crucial. If too high, it can burn out the pigment and change coating viscosity, and if too low it may "kick out" resin and pigment from the water and leave pigment deposits. Resolubility problems in waterborne inks are primarily due to lack of a resin system being totally soluble in water. Some waterborne inks require use of organic cosolvents to achieve low enough surface tensions to wet certain substrates.

Pigments possess a range of properties that influence bond strength, adhesion, pH stability, viscosity, color and coatability. Important attributes of binders include the ability to carry and disperse a range of pigments, to wet low surface energy substrates, to enhance coatability and drying, and to increase adhesion to substrates. Organic solvents, such as alcohols, glycols, and glycols ethers, can assist in adjustment of drying speed, controlling foam, and lowering of surface tension. Additives can act as adhesion promoters or bonding agents, particularly if pigment colors detrimentally influence the bonding and adhesive properties of the formulation. All of these formulation variables influence surface tension, and the coating will wet the substrate only if the surface tension is lower than the wetting tension, or critical surface energy, of the substrate. This does not guarantee that the ink will necessarily adhere to a substrate that it wets, but verifying that this requirement is met is certainly a crucial step in the right direction.

## Surfactant Performance



Ink formulators can plot the overall performance of surfactants by measuring and characterizing them in three dimensions; with respect to surface tension, concentration, and diffusion time (surface age). This can be done manually, or with a series of dynamic surface tension runs at increasing surfactant concentrations, using a SensaDyne maximum bubble pressure tensiometer and automatic dispensing system. The result is a three-dimensional plot, as shown in Figure 2. This technique can also be used on surfactant-containing ink formulations to see effects of formulation changes. Non-active additives primarily shift the plot upward or downward, while changes in type of surfactant or concentration tilt and/or shift the plot.

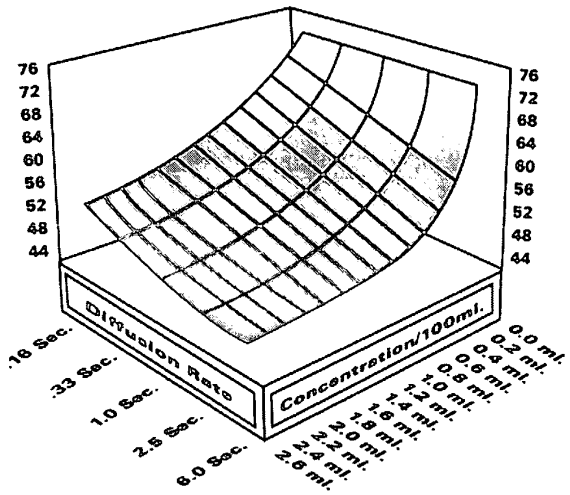
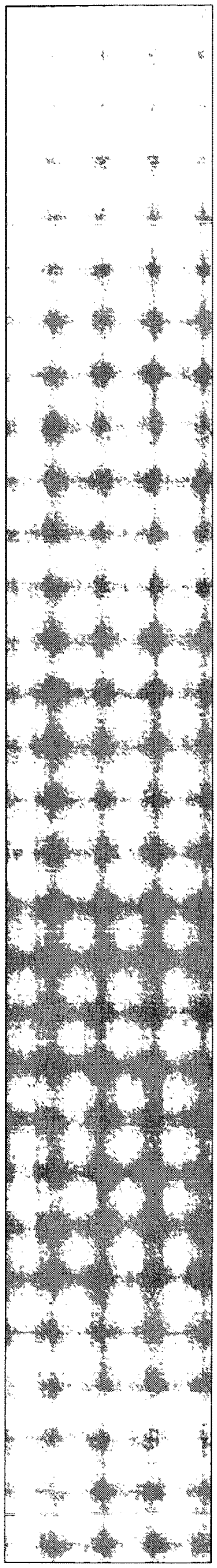


Figure 2 / Three-Dimensional Fluid Characteristics

Surfactants that diffuse slowly may not lower surface tensions sufficiently, within dynamic coating time constraints, to acceptable levels and may be partially responsible for defects such as: Bénard cells (hexagonal cells with well marked centers produced by circulation patterns in thin films); craters (bowl-shaped depressions) or pin holes; crawling or retraction (dewetting of the applied coating); floating (mottled, blotchy, or streaked appearance); orange peel (surface bumpiness); and picture framing (edge buildup). Both rheology and surface tension modifications are used to reduce or eliminate surface defects. Increasing the viscosity can eliminate retraction, for example, but if a viscosity increase is not viable, then the formulator may have to address defect reduction through surfactant modification.

A rapidly diffusing surfactant can mitigate surface defects by eliminating surface tension gradients. This occurs through rapid surfactant migration from high concentrations (low surface tension) to low concentrations (high surface tension). Formulators will sometimes mistakenly increase surfactant concentration in order to reduce gradients, rather than use a better surfactant. This can result in higher surfactant costs and other problems. A surfactant having both low equilibrium and dynamic surface tension in water may not necessarily have the same characteristics in a highly formulated system. Extra surfactant can become "tightly bound" with polymeric binders, or can be solubilized with pigment micelles, becoming ineffective in producing further surface tension reduction.

Some classes of surfactants have rapid diffusion characteristics because of unique polar molecular structures. This type of surfactant is capable of reducing surface tension with the extra benefit of reducing or preventing foam. Hydrophobe-hydrophile-hydrophobe structures, which displace materials that form solid structural films at the interface, make excellent wetting agents or surface tension reducers. These acetylenic diol-based surfactants have highly branched alkyl groups and are horizontally, rather than vertically, adsorbed at the air/liquid interface. At low concentrations these molecules cover large areas, but can be squeezed together as the concentration increases, exhibiting a unique compressible nature. The centrally located hydrophile gives the molecule a flat surface orientation,



while the hydrophobic chain groups minimize intermolecular attraction, which contributes to low-foaming/defoaming capability. The disadvantage of a surfactant that only lowers surface tension is that separate defoamers may have to be added, which can themselves contribute to surface defects. Formulators should try to use a suitable surfactant that ideally has both low equilibrium and low dynamic surface tension values — low enough so that the coating is applied to the substrate at process speeds with a desirable viscosity. It is ideal if the surfactant used can perform more than a single function.

## Surface Energy

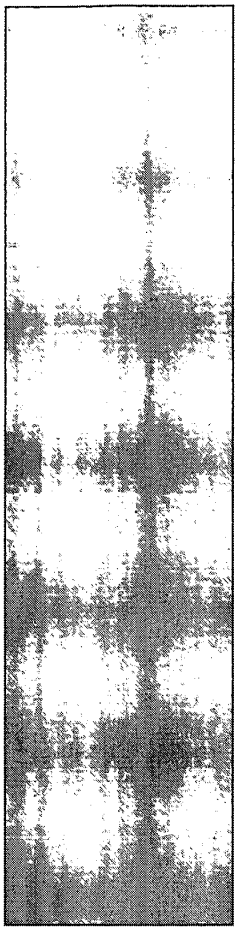
Transfer and spreading of an ink on a substrate depends on the surface energy of the material delivering the ink, the surface tension of the ink, and the surface energy of the substrate receiving the ink. The substrate must have a surface energy higher than the ink, with forces of attraction great enough to promote good transfer and spreading, which in turn facilitates good adhesion. Additional factors affecting adhesion include release properties of the surface, substrate composition, and the structure of the substrate layer.

| Formamide Volume (%) | Ethyl Cellosolve Volume (%) | Wetting Tension Dynes/Cm |
|---|---|---|
| 0 | 100.0 | 30 |
| 2.5 | 97.5 | 31 |
| 10.5 | 89.5 | 32 |
| 19.0 | 81.0 | 33 |
| 26.5 | 73.5 | 34 |
| 35.5 | 65.0 | 35 |
| 42.5 | 57.5 | 36 |
| 48.5 | 51.5 | 37 |
| 54.0 | 46.0 | 38 |
| 59.0 | 41.0 | 39 |
| 63.5 | 36.5 | 40 |
| 67.5 | 32.5 | 41 |
| 71.5 | 28.5 | 42 |
| 74.7 | 25.3 | 43 |
| 78.0 | 22.0 | 44 |
| 80.3 | 19.7 | 45 |
| 83.0 | 17.0 | 46 |
| 87.0 | 13.0 | 48 |
| 90.7 | 9.3 | 50 |
| 93.7 | 6.3 | 52 |
| 96.5 | 3.5 | 54 |
| 99.0 | 1.0 | 56 |

Figure 3 / Mixtures Used in Measuring Wetting Tension Solutions

Measuring the wetting tension, or surface energy, of substrates is commonly and inexpensively done with the use of "dyne liquid" solutions. These are purchased as a series of premixed solutions, each of a given wetting tension in dynes/cm. Users can also prepare their own solutions using a set of reagents, such as formamide (HCONH2) and Union Carbide's ethyl Cellosolve® [ethylene glycol monoethyl ether (CH3CH2OCH2CH2OH)]. These particular non-active wetting solutions are prepared by mixing the two in proportions as designated in ASTM D 2578-84. This allows a series of wetting solutions to be formulated in a range from 30 to 56 dynes/cm, based on the proportions, as shown in Figure 3. To make drops or thin films more discernible, ASTM recommends adding a small amount of highly tincted dye. The ASTM method requires narrow standard temperature (23±2°C) and relative humidity (50±5%) test conditions, due to the inverse temperature/ surface tension relationships of liquids.

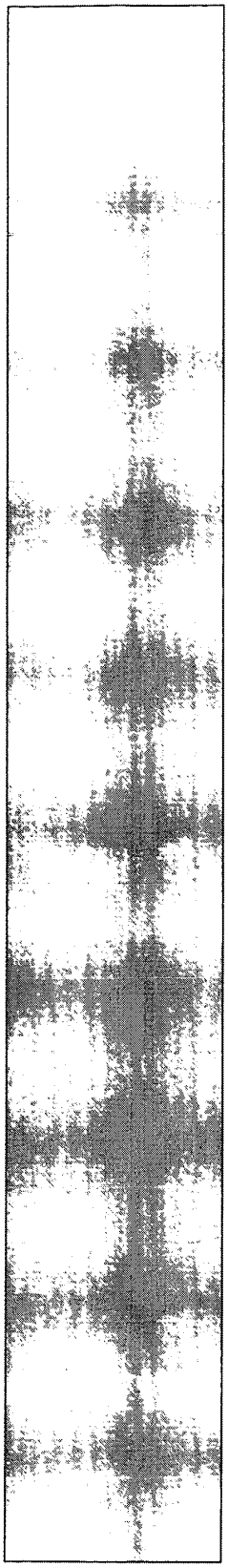
The dyne liquid solution (DLS) must readily wet the surface for the substrate material to be at a wetting tension equal to the surface tension of the DLS used. The ASTM method clarifies this as a continuous one square inch film that remains intact for at least two seconds. If the liquid film spreads readily, then a higher surface tension DLS is needed. If the DLS breaks into droplets (beads up) then a lower surface tension DLS is needed. The user arrives at the equivalent surface energy value of the substrate, when the DLS remains spread out but has no particular tendency to bead up or spread further. Working upward, toward higher surface tensions, is recommended by the



ASTM standard because wetability is easier to see than non-wetability. Problems with DLS formulations, whether purchased or mixed, can result when reagents are not immediately used, as they have a finite "shelf life." Surface tensions will change due to contamination and/or evaporation. For example, ethyl Cellosolve is more volatile than formamide. When these two reagents are utilized, the lower dyne solutions that contain a greater percentage of ethyl Cellosolve are more susceptible to evaporation and a resultant increase in surface tension, a problem verified in long term studies of wetting tension solutions.

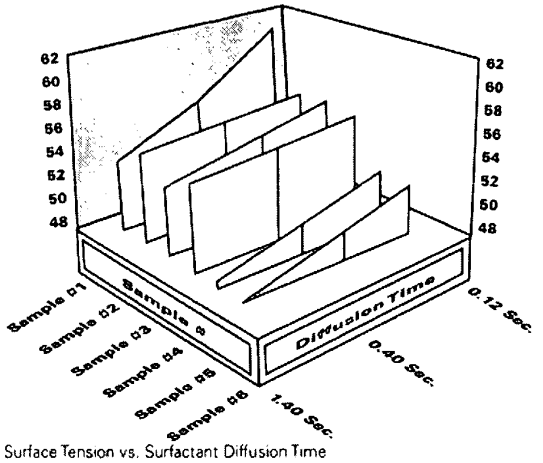
Maximum bubble pressure tensiometers can verify purchased DLS formulations and simplify the two-reagent method. Starting with a test solution of 100% ethyl Cellosolve (30 dynes/cm) and progressively adding formamide to increase the surface tension of the test solution, sequential testing of the substrate is done. Surface tension is measured before each progressive test, or at the end when the final mixture is judged to adequately wet the substrate. This final surface tension value is equal to the wetting tension of the substrate. This works well for surface tensions up to 40 dynes/cm, where the ratio ends up roughly two thirds formamide and one third ethyl Cellosolve. If the substrate wetting tension is suspected to be above 37 dynes/cm it is faster to start with a one to one ratio.

This method eliminates the need to use additional, often expensive and complex contact angle measuring instruments that are used to determine wetting tensions. Another advantage of using the SensaDyne tensiometer, since temperature is measured along with surface tension, is that wetting tensions can be determined under ambient conditions, out on the factory floor, for example, without needing an environmental test chamber. With the tested substrate most likely at ambient temperature and humidity, the surface tension reading of the DLS gives the surface energy at ambient (for which wetting tension is most pertinent) under conditions in which the printing process is most likely to take place.



## Summary

Instruments located adjacent to formulation or press sites must be simple to use, be suitable for both dynamic and static surface tension measurement, and not be effected by contaminants and any adverse site conditions.




Surface Tension vs. Surfactant Diffusion Time

**SensaDyne 6000 Surface Tensiometer Test Summary : Water-Based Inks**

| Test Sample # (All tests at 25.0 degrees C) | | Test #1 | Test #2 | Test #3 |
|---|---|---|---|---|
| Sample #1 - | Surface Tension - Dynes/Cm | 52.9 | 56.3 | 62.0 |
| | Diffusion Rate - Seconds. | 1.30 | 0.41 | 0.13 |
| Sample #2 - | Surface Tension - Dynes/Cm. | 54.8 | 55.5 | 55.8 |
| | Diffusion Rate - Seconds. | 1.48 | 0.41 | 0.12 |
| Sample #3 - | Surface Tension - Dynes/Cm. | 52.5 | 54.0 | 55.7 |
| | Diffusion Rate - Seconds. | 1.40 | 0.38 | 0.12 |
| Sample #4 - | Surface Tension - Dynes/Cm. | 54.3 | 55.1 | 55.4 |
| | Diffusion Rate - Seconds. | 1.45 | 0.43 | 0.12 |
| Sample #5 - | Surface Tension - Dynes/Cm. | 46.6 | 48.6 | 51.1 |
| | Diffusion Rate - Seconds. | 1.24 | 0.36 | 0.13 |
| Sample #6 - | Surface Tension - Dynes/Cm. | 46.2 | 47.7 | 50.5 |
| | Diffusion Rate - Seconds. | 1.24 | 0.36 | 0.11 |

Figure 4 / Water-Based Inks

SensaDyne's dynamic surface tension measurement technique is based on a patented modification of the maximum bubble pressure method. Two probes with 4.0 mm and 0.5 mm orifices are inserted into a fluid. The computerized instrument measures maximum differential bubble pressure at the orifices and calculates the fluid surface tension. Bubbling within the body of the fluid makes the system immune to surface contaminants and surface foam. The instrument is calibrated by pre-testing two fluid standards of known surface tension values, such as deionized water and alcohol. Immersing the probes in the middle of a sample is the extent of the expertise demanded of the user.

Surface tension values are used to compare the quality of newly formulated inks against previously measured inks. DLS wetting tensions are used to determine and compare new versus previously used substrates. Information can be obtained for three-dimensional characterization of active surfactant-containing formulations when the concentration of the surfactant or other additives is changed. Dynamic surface tension curves for a series of inks with active surfactants are illustrated in Figure 4. Formulations that exhibit both low equilibrium and low dynamic values can be determined prior to their use.

Comparing the data and dynamic curves of the first three water-based inks (Sample #1 through #3) in Figure 4, reveals that Sample #1 has a fairly steep dynamic curve that should give the lowest equilibrium surface tension once the curve flattens (to the left) and reaches its minimum value, at some time slower than the tested 1.4 seconds. However, it has the highest dynamic value (62) of the three at a surface age of 0.12 seconds. Sample #2 has the smallest slope, and would have the lowest dynamic value if the diffusion time allowed were much less than 0.12 seconds.

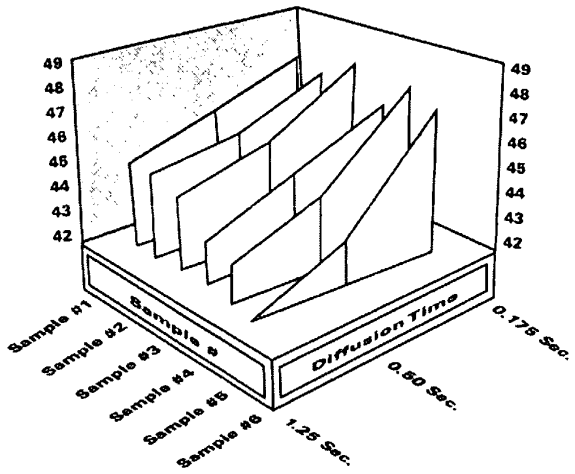



Figure 5 / Fountain Solutions

Within the tested surface ages, however, Sample #3 has both the lowest equilibrium (52.5) and dynamic (55.7) surface tension values. It could be the best choice of the three, all other factors being equal. Comparing the last three formulations (Sample #4 through #6) in Figure 4 reveals Sample #4 as being the best candidate for any process in which the surface age is limited to 0.12 seconds or less. A similar analysis can be performed on a series of fountain solutions, as shown in Figure 5.

Formulation and coating problems can be greatly mitigated, or avoided entirely, by measuring surface tensions and wetting tensions of the companion substrates before the inks are used. Press site adaptable instruments allow faster and more positive problem mitigation by allowing changes to be verified and quantified immediately after formulation adjustments have been made. Formulators can improve transfer, spreading, and adhesion of inks by choosing surfactant and additive combinations that provide the best surface tension profiles for the application.

For more information on surface-tension measurement, contact SensaDyne Instruments, Chem-Dyne Research Corp., 2855 E. Brown Road, Suite 20, Mesa, AZ 85213.




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# Selecting Laminating Adhesives

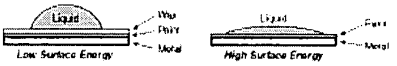
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Surface contact is fundamental to adhesive performance. The ability to get intimate surface contact is a function of the substrate's surface energy and texture, as detailed below.

## Surface Energy

Adhesion is the molecular force of attraction between unlike materials. The strength of attraction is determined by the surface energy of the material. The higher the surface energy, the greater the molecular attraction. The lower the surface energy, the weaker the attractive forces. In other words, on a high surface energy material, the adhesive can flow (or "wet-out") to assure a stronger bond. High surface energy materials draw the adhesive closer for high bond strength.

The difference is similar to the behavior of water on the finish of a car. On a newly waxed car, water beads up (low surface energy) and on an older finish it wets out (high surface energy).




Surface energy is measured by dynes per centimeter. The dyne level is the actual reading of the critical surface area. The chart below compares the relative surface energy of commonly used substrates. On low surface energy plastics, select an adhesive designed to "flow out" on low surface energy plastics. On high surface energy plastics choose a "harder" adhesive designed for that purpose.




## Texture

It's a common misconception that more adhesive means better adhesion. On smooth surfaces, good surface contact can be achieved with relatively thin layers of adhesive, typically 2 mils. On rough or textured surfaces, more adhesive is required to fill in the hills and valleys, typically 5 mils.

| | ***High Surface Energy Substrates*** | ***Low Surface Energy Substrates*** |
|---|---|---|
| |  |  |
| ***Rough/ Textured Surfaces*** | Thick .005" adhesive<br>#200 adhesive<br>ie. 468 | Thick .005" adhesive<br>#300 adhesive<br>ie. 9472 |
| ***Smooth Surfaces*** | Thick .002" adhesive<br>#200 adhesive<br>ie. 467 | Thick .002" adhesive<br>#300 adhesive<br>ie. 9471 |

| Substrates Greater Than 37 dynes/cm | Substrates Less Than 37 dynes/cm |
|---|---|
| METALS:<br>Aluminum, Copper, Glass, Lead, Stainless Steel, Tin, Zinc<br><br>PLASTICS:<br>ABS, Acrylic, Alkyd Enamel, Epoxy Paint, Kapton® (Polymide), Noryl®, Nylon, Phenolic,<br>Polane® Paint, Polycarbonate, Polyester, Polyurethane Paint, PVC (Polyvinyl Chloride) | Acetal, EVA, Polyethylene, Polypropylene,<br>Polystyrene, PVA, Tedlar®, Teflon®<br><br>Back to top of page |



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# Substrate's Dynes/Cm

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## High Surface Energy Substrates
### (Greater Than 37 dynes/cm)

| Dynes/cm | METALS |
|---|---|
| 1103 | Copper |
| 840 | Aluminum |
| 753 | Zinc |
| 526 | Tin |
| 458 | Lead |
| 700-1100 | Stainless Steel |
| 250-500 | Glass |

| Dynes/cm | PLASTICS |
|---|---|
| 50 | Kapton® (Polymide) |
| 47 | Phenolic |
| 46 | Nylon |
| 45 | Alkyd Enamel |
| 43 | Polyester |
| 43 | Epoxy Paint |
| 43 | Polyurethane Paint |
| 42 | ABS |
| 42 | Polycarbonate |
| 39 | PVC (Polyvinyl Chloride) |
| 38 | Noryl® |
| 38 | Acrylic |
| 38 | Polane® Paint |

## Low Surface Energy Substrates
### (Less Than 37 dynes/cm)

| Dynes/cm | |
|---|---|
| 37 | PVA |
| 36 | Polystyrene |
| 36 | Acetal |
| 33 | EVA |
| 31 | Polyethylene |
| 29 | Polypropylene |
| 28 | Tedlar® |
| 18 | Teflon® |

These values are provided as a guide. Modifications in formulations can substantially alter surface energies.

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